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One-Pot Catalytic Conversion of Raw Lignocellulosic Biomass into Gasoline Alkanes and Chemicals over $LiTaMoO_6$ and Ru/C in Aqueous Phosphoric Acid

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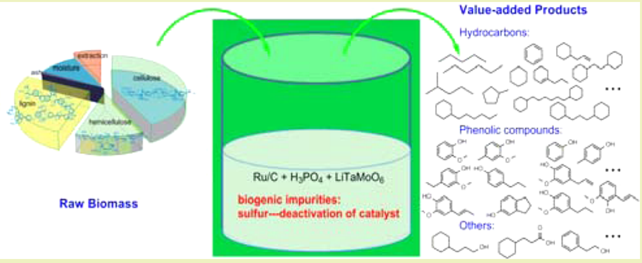
Supporting Information

ABSTRACT: Lignocellulosic biomass is a renewable feedstock that has the potential to replace the diminishing fossil fuels. Herein, we reported the simultaneous conversion of cellulose, hemicellulose and lignin from raw biomass into gasoline alkanes (hexanes and pentanes) and monophenols and related hydrocarbons over layered $LiTaMoO_6$ and Ru/C in aqueous phosphoric acid medium. Specifically, gasoline alkanes were directly yielded from the carbohydrate components, based on hemicellulose and cellulose, and the total yield could be up to 82.4%. Notably, the lignin fraction could also be transformed into monophenols, related alcohols and hydrocarbons by the one-pot reaction. It suggested that the hydrocracking of monophenol fraction could be performed in this catalytic system. The total yield of volatile products was 53% based on the lignin fraction. In this paper, the influences of phosphoric acid concentration, substrate ash and the amino acids derived from the biogenic impurities were investigated and different raw biomass substrates were tested. Furthermore, the catalysts could be reused for several runs to convert raw biomass without pretreatment.



KEYWORDS: *Lignocellulosic biomass, Gasoline alkanes, Phenols, Layered compounds, Catalytic conversion*

■ INTRODUCTION

Increasing interest has been paid to the sustainable fuels and chemicals from lignocellulosic biomass. To maintain the balance between the increasing demand of fuels and chemicals and the depletion of resources, and to mitigate carbon dioxide emissions, research efforts and programs have been developed to transform raw biomass into valuable products.[1−3] Biomass conversion to fuels is presented as one of the promising routes of biomass utilization.[4] To realize this route, many approaches were introduced, such as hydropyrolysis[5−9] and catalytic conversion of carbohydrates,[10−12] alcohols[13,14] as well as furans.[15,16] The hydrocarbon products include aromatics, long-chain hydrocarbons (C_{7+}) and gasoline alkanes. For instance, direct catalytic conversion of carbohydrates or related alcohols mainly produced gasoline alkanes that include hexanes and pentanes (*n*-hexane, *n*-pentane and their isomers).[10−14,17−19]

It is known that cellulose and hemicellulose consist of C_6 and C_5 sugar units, both of which are linked by ether bonds. Therefore, direct hydrodeoxygenation of cellulose or hemicellulose would lead to the formation of gasoline alkanes. However, selective removal of oxygen from cellulose or hemicellulose without C−C bonds breaking remains a challenge, especially when rigid cellulose was used as the substrate. Recently, progress on hydrodeoxygenation of cellulose to hexanes has been made.[8,10,11,20] Ribeiro and coworkers studied fast-hydropyrolysis of cellulose and poplar, approximately 55% and 32% C_{4+} hydrocarbons were achieved, respectively.[8] Tomishige et al. reported the production of *n*-hexane from cellulose over Ir-ReO_x/SiO_2 and H-ZSM-5 catalysts in water/*n*-dodecane biphasic solvent.[12] The proposed reaction pathway was named as the sorbitol route: hydrolytic hydrogenation of cellulose to sorbitol and subsequently hydrogenolysis of sorbitol to *n*-hexane. Sels and co-workers investigated conversion of cellulose to gasoline alkanes (*n*-hexane, methylcyclopentane and *n*-pentane) by using $H_4SiW_{12}O_{40}$-modified Ru/C (htRu/C) and $H_4SiW_{12}O_{40}$ catalytic system in water/*n*-decane.[11] In contrast, they proposed

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gasoline alkanes were mainly yielded from a different route, which they called the HMF (5-hydroxymethylfurfural) route. In this route, HMF, produced from dehydration of cellulose derived glucose, was the main intermediate that was transformed into gasoline alkanes via consecutive hydrogenation/hydrogenolysis.[11,21−25] Although a biphasic system may function to separate intermediates or products, or to suppress undesirable reactions,[11] the aqueous phase should be fully addressed as the solvent because it is readily available. Therefore, we employed the Ru/C + layered compound + phosphoric acid system to convert directly cellulose into hexanes in aqueous phase.[20] In this system, isosorbide was the most robust intermediate, which corresponded to former studies.[11,17,26] Numerous research efforts suggested Ru/C catalyzed hydrogenation and acid-catalyzed hydrolysis and dehydration played important roles in the formation of alkanes.[11,27−31] But the addition of layered compounds was crucial because they could dramatically suppress the formation of isosorbide.[20,32]

Although a promising yield of hexanes could be achieved by direct catalytic reactions, the feedstocks, such as cellulose, glucose and sorbitol, required separation or reaction from raw biomass. On the contrary, large-scale commercial production would address the significance of raw biomass as the feedstock. Pyrolysis or hydropyrolysis of biomass toward liquid fuel was a promising route;[8,33−36] catalytic conversion of biomass to gasoline alkanes should not be underestimated for its high carbon efficiency.[11] Sels and co-workers used the same catalytic system of htRu/C+$H_4SiW_{12}O_{40}$ to convert softwood to gasoline alkanes with a yield of 60%.[11] Apart from cellulose and hemicellulose, lignin, on the other hand, is an amorphous, highly crossed-linked polymer that consists of phenyl propylene units. Lignin is the most abundant source of aromatic compounds that should be fully exploited to produce aromatics or fuels. Lots of studies have been dedicated to lignin degradation through catalytic conversion process.[37−41] Although these studies achieved valorization of lignin, simultaneously catalytic conversion of carbohydrates and lignin could show significant advantage for commercial utilization.[42−44] In the case of one-pot conversion of raw biomass, Zhang and co-workers used the Ni−W_2C/AC catalyst to hydrocrack woody biomass into chemicals, mainly ethylene glycol, other diols, and monophenols.[43] Ford and co-workers employed Cu20-PMO as the catalyst to convert woody biomass to alcohols in the supercritical methanol medium.[44] Very recently, Sels's group reported a catalytic biorefinery process to valorize fully polysaccharide and lignin from birch sawdust to high yields of value-added chemicals, specifically 92% of carbohydrates based on initial polysaccharide components and 50% of phenolic monomers and 20% of phenolic dimers based on lignin content, by employing Ru/C as the catalyst in methanol.[42] They suggested high phenolic monomers yield resulted from high syringly unit lignin because they lack free ortho-positions.[42] However, to the best of our knowledge, no report has achieved one-pot transformation of raw biomass into gasoline alkanes and lignin-derived products, simultaneously.

This paper demonstrated a route to convert various raw and untreated lignocellulosic feedstocks into value-added chemicals and hydrocarbons over Ru/C combined with $LiTaMoO_6$ in low concentration of phosphoric acid solution. The carbohydrate fraction was selectively transformed into gasoline alkanes that were mainly hexanes and pentanes. For the lignin part, monophenols and its derived alcohol and hydrocarbons were formed after the test. Different feedstocks were used in this research. The effects of biogenic impurities such as amino acids and ashes, and the concentration of phosphoric acid solution were discussed in detail, which have not been systematically studied before. Amino acid with sulfur was demonstrated to result in deactivation of catalysts. In contrast, ashes did not show a negative effect on our catalytic system, though much research demonstrated that ash might be responsible for catalyst deactivation.[45−47] The one-pot conversion of raw biomass would bring us a potentially commercial application for efficient production of gasoline alkanes and chemicals from abundant biomass.

EXPERIMENTAL SECTION

Materials. Pine sawdust, corn stalk, wheat straw, rice straw and corncob were obtained from Guangdong province, China. After dried at 323 K for 24 h, they were milled and screened into powders with size 60−80 meshes before use. Microcrystalline cellulose (Crystallinity 81%, degree of polymerization 220) was purchased from Alfa Aesar and was directly used. 5 wt % Ru/C, xylose, methionine, tryptophan, HMF, Li_2CO_3, MoO_3, Ta_2O_5, 2-methylpentanoic acid, 1-hexanol, 1-pentanol, 1-hexanoic acid, hexitols, alkali lignin and γ-caprolactone were purchased from Aladdin. Phosphoric acid was supplied by Tianjin Fuyu Fine Chemical Co., Ltd.

Raw Biomass Feedstock Analysis. Different feedstocks were characterized by a Nicolet iS50 FT-IR spectrophotometer (Fourier transform infrared spectrometer, Thermo Scientific, USA) through the KBr pellet method. The components of lignocellulosic biomass were determined by using the analytical methods of the U.S. National Renewable Energy Laboratory (NREL).[48] The contents of C, H, N and S in raw biomass and lignin were determined by using a Vario EL Z elemental analyzer (Elementar Analysensysteme, Hanau, Germany).

Process for Conversion of Raw Biomass. The catalytic conversion of raw biomass was performed in a 100 mL stainless steel autoclave. Typically, 1.0 g of feedstock, 0.2 g of 5 wt % Ru/C, 0.2 g of $LiTaMoO_6$ and 40 mL of phosphoric acid solution were loaded into the autoclave. The autoclave was purified by N_2 for three times and then pressurized with 6 MPa of hydrogen (RT, room temperature). After the designated temperature was reached, the reactor was kept at a stirring rate of 450 rpm for a certain time. When the reaction was finished, the reactor was cooled to 383 K within 10 min and the gas samples were collected at the stable temperature. After that, the autoclave was cooled to room temperature within 15 min. All the experiments were performed three times.

For the recycling potential test of the catalyst, the catalysts and the unreacted substrate were separated by filtration. Then the solid was washed with hot water. After dried in air at 343 K overnight, it was added into the reactor for the next run. Fresh phosphoric acid solution and pine sawdust were loaded. For the FT-IR test, the solid was washed with CH_2Cl_2 and hot water repeatedly for three runs, and then dried before the test.

Products Separation and Analysis. After reaction, the liquid products were separated by extraction and the extractant was ethyl ether. The water-undissolved products such as monophenols, hydrocarbons and some alcohols were diffused into the ethyl ether phase, whereas other products like sorbitol, isosorbide and sorbitan remained in the water phase.

The collected gas samples from biomass conversion were analyzed and quantified by a gas chromatogram (Agilent 7890A TCD-FID detector, external standard method). The ethyl ether fraction was quantified by an internal standard method (standard: acetophenone). An Agilent 7890A-5975C inert MSD was used to analyze the ethyl ether fraction and the products were identified based on the NIST MS library (column: HP-INNOWAX, 30 m × 0.25 mm × 0.25 μm). For the water-dissolved products, a waters e2695 equipped with a Waters 2489 UV/vis detector (wavelength: 284 nm) and a Waters 2414 refractive index detector was used to qualify the concentration (external standard method). The Shodex SUGAR SH1011 was the

Table 1. Conversion of Different Substrates over $LiTaMoO_6$ and Ru/C in Aqueous Phosphoric Acid[a]

				yield[b] (%)										
				based on cellulose and hemicellulose							based on lignin			
entry	substrate	T [K]	T [h]	n-hex	MCP	i-hex	C5A	gasoline	C1−C4A	other	sum	phenol	other LDP	sum
1	xylose	503	24	0.7	0.1	0	48.1	48.9	2.2	35.8	86.9	ND	ND	0
2	cellulose	503	24	45.6	7.0	1.0	4.1	57.7	6.3	28.7	92.7	ND	ND	0
3[c]	pine sawdust	503	24	0	0	0	0	trace	0	trace	trace	0	0	trace
4		503	12	37.9	10.5	2.2	11.8	62.4	9.2	24.3	95.9	13.3	2.0	15.3
5		503	24	47.1	12.6	3.1	16.9	79.7	9.9	17.1	106.7	16.2	5.0	21.2
6	corn stalk	503	12	29.4	8.1	0.7	13.8	52.0	5.8	7.2	65	16.2	3.7	19.9
7		503	24	43.5	15.2	1.7	22.0	82.4	9.2	8.7	100.3	23.8	11.9	35.7
8	corncob	503	12	27.9	9.1	0.8	20.9	58.7	4.5	8.1	71.3	18.6	4.0	22.6
9		503	24	33.1	10.5	1.2	23.8	68.6	5.9	12.1	86.6	35.4	16.0	51.4
10	wheat straw	503	12	16.1	6.9	0.9	8.3	32.2	4.6	7.8	44.6	12.6	4.6	17.2
11		503	24	19.9	7.8	1.2	9.9	38.8	8.7	7.2	54.7	21.4	17.6	39.0
12	rice straw	503	12	16.6	6.1	1.1	7.2	31.0	8.1	7.6	46.7	16.4	3.1	19.5
13		503	24	21.2	6.8	1.5	11.6	41.1	9.8	12.7	63.6	18.3	13.8	32.1
14	pine sawdust	443	24	15.9	4.3	0.6	2.5	23.3	2.1	34.2	59.6	2.2	3.9	6.1
15		463	24	34.2	9.8	1.3	9.9	55.2	5.3	27.0	87.5	3.1	5.1	8.2
16		483	24	36.4	10.2	1.9	10.2	58.7	6.5	23.0	88.2	7.2	5.6	12.8
17[d]	alkali lignin	503	24	ND	ND	ND	ND	0	0	trace	trace	11.7	2.8	14.5
18[e]	GCL	503	24	21.1	1.8	1.0	3.0	26.9	0.6	57.8	85.3	ND	ND	0
19[f]	HA	503	24	41.8	1.4	5.1	2.9	51.2	1.7	41.3	94.2	ND	ND	0
20[g]	MPA	503	24	9.9	0.1	32.0	3.2	45.2	1.1	50.5	96.8	ND	ND	0
21[h]	HA	503	24	73.2	5.6	4.5	1.1	84.4	0.4	8.1	92.9	ND	ND	0
22[i]	HMF	503	24	31.5	2.5	0.9	14.2	49.1	5.1	25.1	79.3	ND	ND	0

[a] Unless otherwise specified, the reaction conditions were feedstock (1 g), $LiTaMoO_6$ (0.2 g), Ru/C (0.2 g), 0.2 mol/L H_3PO_4 solution (40 mL), 6 MPa H_2 (RT). [b] Products: n-hex = n-hexane; MCP = methylcyclopentane; i-hex = isohexane; C5A = C5 alkanes, mainly n-pentane (99%); gasoline = gasoline alkanes including n-hex, MCP, i-hex and C5A; C1−C4A = alkanes with 1−4 carbon numbers, mainly methane, ethane, propane and butane; other = products based on cellulose and hemicellulose which were detected by GC−MS and HPLC, including 1-hexanol, hexitols, 1-pentanol, acetic acid, hexanoic acid, pentanoic acid, etc.; other LDP = other lignin-derived compounds that include benzene in the gas phase, hydrocarbons, ether, alcohols, acid detected by GC−MS; ND = not determined. In the yield section, negligible yield of CO_x was not added (<1%). The sum of the yield over 100% (based on cellulose and hemicellulose) might be resulted from that some of the products (for instance, acetic acid, a small amount of alkanes) were yielded from lignin. [c] In this test, no catalyst was loaded and the liquid phase was 40 mL water. [d] The substrate was 0.2 g of alkali lignin. [e] The GCL conversion was 89%; the yields for 1-hexanol and hexanoic acid were 18.5% and 37.9%, respectively. [f] The HA conversion was 99.9%; the yield for 1-hexanol was 38.5%. [g] The MPA conversion was 99.9%; the main gas product was 32% isohexane; the yield for 2-methylpentanol was 44.5%. [h] 0.2 g of HA, conversion was 99.9%; the yield for 1-hexanol was 6.5%. [i] 0.2 g of HMF, conversion was 99.9%.

column that was maintained at 323 K. 10 mM aqueous sulfuric acid solution was used as the mobile phase and the flow rate was 0.5 $mL\cdot min^{-1}$.

Catalyst Preparation and Characterization. The stoichiometric mixture of Li_2CO_3, MoO_3 and Ta_2O_5 was calcined at 873 k for 24 h to synthesize $LiTaMoO_6$. A Philips XL30 equipped with energy dispersive spectroscopy (EDS) was used to analyze the morphological information (SEM, scanning electron microscopy). SEM and FT-IR (KBr pellet method) were also used to characterize the $LiTaMoO_6$. Besides that, an XPert Pro MPD (Philip) equipped with a Cu Kα radiation (λ = 0.154 nm, operating at 100 mA and 40 kV) was used to record the X-ray diffraction (XRD) pattern of $LiTaMoO_6$. After the reaction, the residue fraction after washed with water was analyzed through SEM-EDS characterization. Inductively coupled plasma-atomic emission spectrometry (ICP-AES, OPTIMA 8000) was introduced to detect the leaching of the catalyst.

Equations. The conversion was calculated based on the difference of weight before and after the reaction, as displayed by eq 1:

$$\text{conversion (\%)} = \frac{W_b - W_a}{W_b} \times 100\% \tag{1}$$

where W_b denotes the weight of the feed before the reaction and W_a denotes the weight of the feed after the reaction.

The yields of the products were determined by the following equations:

$$\text{yield of lignin derived products (\%)} = \frac{M_{cp}}{M_{cf}} \times 100\% \tag{2}$$

$$\text{yield of cellulose and hemicellulose derived products (\%)} = \frac{M_{cp}'}{M_{cf}'} \times 100\% \tag{3}$$

where M_{cp} denotes the mass of carbon in the products from lignin. In this report, the lignin derived products included phenolic compounds and other volatile aromatic compounds. M_{cf} denotes the mass of carbon in the lignin that was measured by the CHNS analyzer. For the cellulose and hemicellulose parts, M_{cp}' denotes the mass of carbon in the products from cellulose and hemicellulose that included the gas phase products-alkanes, and the liquid products that are excluded from the lignin derived products. M_{cf}' denotes the mass of carbon in the cellulose and hemicellulose of the feedstock.

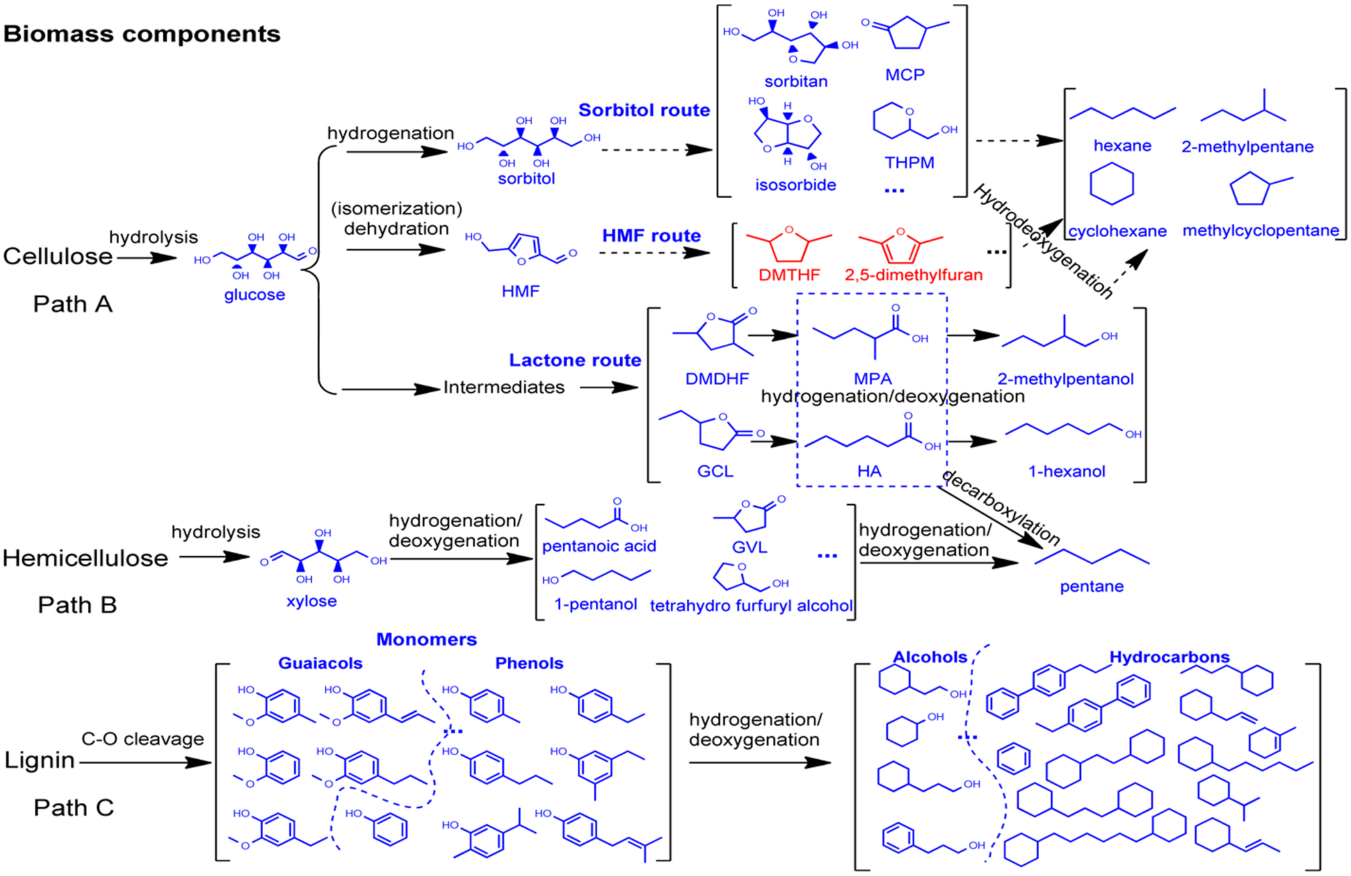
For the selectivity of Table 1, entries 18−20:

$$\text{gas phase selectivity (\%)} = \frac{\text{C mass in hexanes and pentanes}}{\text{C mass in all alkanes}} \times 100\% \tag{4}$$

RESULTS AND DISCUSSION

Conversion of Raw Biomass. Our recent study suggested that cellulose could be converted to hexanes over the Ru/C

Scheme 1. Proposed Routes for the Conversion of Raw Biomass[a]



[a]Blue, detected; red, not detected.

combined with layered compounds such as $LiNbMoO_6$ in aqueous phosphoric acid under hydrogen atmosphere.[20] Ru/C showed high hydrogenation and hydrogenolysis activity.[20,49] Specifically, when only Ru/C was used as the catalyst, cellulose was almost totally hydrocracked to C1−C4 alkanes. Phosphoric acid promoted cellulose conversion by hydrolysis compared to pretty low conversion when only Ru/C and layered compound were used.[20] With the combination of Ru/C and phosphoric acid, cellulose was mainly converted to isosorbide. However, highest gasoline alkanes yield (72% hexanes and 5.9% pentanes) was obtained over Ru/C + layered compound + phosphoric acid.[20] We proposed the promising yield of hexanes was obtained due to the intercalation effect of the layered compounds which suppressed the formation of the robust byproduct isosorbide.[20] In this work, we also found the layered compound $LiTaMoO_6$ could effectively transform cellulose into hexanes with a good yield of 45.6%, and that of the liquid alkanes was 57.7%, which includes the isomers of hexane and pentane and their cycloalkanes (Table 1, entry 2, and Figure S2 of the Supporting Information). The effective conversion of cellulose to hexanes suggested that layered $LiTaMoO_6$ inhibited the formation of isosorbide. It was revealed by our previous paper and other papers that suggested the layered compounds achieved the inhibition effect.[20,32,50,51] However, more details are needed to disclose the difference of Ta and Nb, which is our next study. Interestingly, when we employed the untreated pine sawdust as the feedstock with a high conversion (Figure S2 of the Supporting Information), high C6 alkanes yields of 62.8% and 16.9% of C5 alkanes were obtained based on the mass of carbon from cellulose and hemicellulose (Table 1, entry 5). The total yield of liquid alkanes could be up to 82.4% when corn stalk was introduced as the feedstock (Table 1, entry 7). It should be noted that some alkanes might be produced from lignin. On the contrary, the reaction could only yield trace alkanes if the catalyst were not used (Table 1, entry 3).

Previous studies disclosed that with a proper catalytic system, cellulose can be selectively transformed into hexanes without the C−C cracking reactions.[10,11] There are two main routes were proposed: the sorbitol route by Tomishige[10] and the HMF route by Sels.[11] In the acidic aqueous medium, the most efficient way to increase the yield of hexanes is to limit the formation of the robust isosorbide. In this work, many intermediates were detected. For instance, in the aqueous phase, HMF, 1-hexanol and hexitols (sorbitol, sorbitan and isosorbide) were detected by HPLC (Figure S7 of the Supporting Information). With the help of GC−MS analysis, 1-hexanol, hexanoic acid, 2-methylpentanoic acid (MPA) and 3,5-dimethyldihydrofuran-2(3*H*)-one (DMDHF) were found in the ethyl ether phase of all these tested raw biomass samples (Figures S10−S17 of the Supporting Information). Most of those intermediates had been analyzed by the group of Sels, and an extensive study of their reactivity and mechanism was performed.[11] However, we also detected the existence of 2-methylcyclopentanone (MCP, Figure S16 of the Supporting Information), tetrahydropyran-2-methanol (THPM, Figure S10 of the Supporting Information) and γ-caprolactone (GCL, Figure S17 of the Supporting Information). These liquid products might be the C6 intermediates to produce hexanes

Table 2. Main Components of Products from Corn Stalk Conversion Corresponding to Entry 7 of Table 1[a]

component[b]	yield (%)	component[c]	yield (%)
phenolic compound	23.84	liquid phase	8.71
phenol, 2-methoxy-	0.45	1-pentanol	1.43
phenol, 2-methoxy-4-methyl-	0.32	1-hexanol	1.48
phenol	1.90	acetic acid	0.15
phenol, 4-ethyl-2-methoxy-	2.46	2(3H)-furanone, dihydro-3,5-dimethyl-	0.15
phenol, 4-methyl-	0.47	2(3H)-furanone, dihydro-5-methyl-	0.11
phenol, 2-methoxy-4-propyl-	6.01	pentanoic acid	2.39
phenol, 4-ethyl-	6.29	pentanoic acid, 2-methyl	0.31
phenol, 4-propyl-	3.23	hexanoic acid	1.05
phenol, 2-ethyl-6-methyl-	0.82	isosorbide	0.08
phenol, 2-methoxy-4-(1-propenyl)-	0.93	sorbitan	0.15
phenol, 4-(3-methyl-2-butenyl)-	0.78	sorbitol	0.17
1H-inden-5-ol, 2,3-dihydro-	0.66	HMF	1.03
phenol, 2-(1,1-dimethylethyl)-4-(1-methylpropyl)-	0.57	levulinic acid	0.11
phenol, 2,6-dimethoxy-4-(2-propenyl)-	0.95	xylitol	0.10
lignin-derived hydrocarbon	10.10	gas phase	91.60
cyclohexane, hexyl-	0.96	methane	1.76
4-propyl-1,1′-biphenyl	4.11	ethane	0.14
benzene (gas phase)	5.03	propane	4.61
lignin-derived alcohol or ether	1.80	butane	2.69
phenylethyl alcohol	0.89	C6A (*n*-hex, MCP and *i*-hex)	60.40
benzene, 1-methoxy-4-pentyl-	0.91	C5A	22.00

[a] Reaction conditions: corn stalk (1 g), $LiTaMoO_6$ (0.2 g), Ru/C (0.2 g), 0.2 mol/L H_3PO_4 solution (40 mL), 6 MPa H_2 (RT), 24 h, 503 K. [b] Based on lignin. [c] Based on cellulose and hemicellulose, the yield of liquid products was the sum of aqueous phase and ethyl ether phase.

through reduction.[12,52] In addition, we did not observe the existence of 2,5-dimethyltetrahydrofuran (DMTHF), which might be caused by that the suggested HMF route is fast or is less favorable in this catalytic system.[53,54] In addition, we also found HMF was most abundant in water phase after reaction, which indicated the difference between our work with Sels's study because the Sels route indicated HMF could be fast converted.[11] Other than HMF, hexitols and THPM were detected that suggested the existence of the sorbitol route confirmed by the studies of Tomishige team, Huber team and Cabiac and co-workers.[10,26,55−57] Besides that, the detectable GCL, DMDHF and MPA might be the intermediates to perform the ring-opening and hydrodeoxygenation reactions for the promising yield of hexanes because Dumesic and co-workers already put forward the catalytic conversion of γ-valerolactone (GVL) to alkenes.[58] In a similar manner, GCL can be transformed into HA or hexanol; and MPA can be yielded from DMDHF. GCL and DMDHF can be produced from cellulose derived carbohydrates.[59,60] Hence, hexane and 2-methylpentane could be formed in the gas phase through hydrodeoxygenation of HA, hexanol, MPA or derived alcohol.

To verify the feasibility of this lactone route, study of these compounds conversion was performed. The results showed that they were selectively converted to hexanes and pentanes with selectivity of 97.8% (GCL), 96.8% (HA) and 97.6% (MPA) (Table 1, entries 18−20). Other than alkanes, the main products in liquid phase were 1-hexanol, 2-methylpentanol or hexanoic acid. Although the hexanes yields were not high, it is undeniable that these tested compounds are the intermediates to produce hexanes from raw biomass.[60] In addition, when the substrate HA was decreased to 0.2 g, high yield of hexanes with 83.3% was achieved. Because these lactone route intermediates were gradually released from the substrate, it was possible that desirable yield of hexanes could be obtained through this route. On the basis of the analysis, therefore, we proposed the alternative ways to produce hexanes (Scheme 1, path A). It should be noted that these intermediates had a low yield (less than 4% for each of them), which suggested they could be easily transformed into hexanes. This observation was comparable to Sels's report which suggested that these intermediates were slowly released from cellulose.[11] In addition, on the basis of our former study[20] and Sels's study,[11] we assumed most of hexanes were produced from HMF route and lactone route in our catalytic system. That was because that sorbitol was easily transformed into isosorbide in the acidic solution. Isosorbide was hardly converted to hexanes, which was confirmed by former studies. Besides that, we could obtain a good hexanes yield of 34% when HMF was introduced as the substrate (Table 1, entry 22).

Apart from the most abundant cellulose, the hemicellulose fraction could constitute more than 25 wt % of the investigated biomass, which reveals it is an importance carbon source (Table S2 of the Supporting Information). The test results of raw biomass conversion with relatively high pentanes yields (compared to cellulose conversion, Table1, entry 2) clearly suggested that it can be efficiently transformed into desired pentanes (Table 1, entries 4−13 and 15−16). GC−MS analysis disclosed that the C5 intermediates included 1-pentanol, GVL and pentanoic acid that could be hydrocracked to pentanes.[61] To validate this hypothesis, xylose, the hemicellulose unit, was introduced to run the conversion test. A good pentanes yield of 48.1% was achieved (Table 1, entry 1). A handful of products in liquid phase were the mentioned C5 intermediates proved the suggested assumption (Scheme 1, path B). In addition, the hydrocracking and decarboxylation of the C6 intermediates should be noted for its potential to yield pentanes.[11]

Lignin, depending on the source, constitutes 10−30 wt % of raw biomass. As a result of its chemical properties and the repolymerization reactions of its degraded monophenols, lignin had been proposed as the most rigid component among the

Table 3. Effect of the Concentration of H_3PO_4 Solution on Raw Biomass Conversion[a]

			yield[b] (%)										
			based on cellulose and hemicellulose								based on lignin		
entry	substrate	$[H_3PO_4]$ [M]	*n*-hex	MCP	*i*-hex	C5A	gasoline	C1−C4A	other	sum	phenol	other LDP	sum
1	pine sawdust	0	5.2	0.9	0	4.1	10.2	19.4	21.0	50.6	2.2	6.6	8.8
2		0.1	32.1	8.0	1.9	13.9	55.9	13.8	18.9	88.6	9.2	5.4	14.6
3		0.2	47.1	12.6	3.1	16.9	79.7	9.9	17.1	106.7	16.2	5.0	21.2
4		0.3	38.1	11.1	2.1	14.3	65.6	8.2	17.6	91.4	20.3	7.6	27.9
5	corn stalk	0	15.1	3.6	0.5	7.6	26.8	1.9	18.6	47.3	12.1	8.7	20.8
6		0.1	36.2	10.6	1.0	16.7	64.5	4.2	13.4	82.1	19.2	10.6	29.8
7		0.2	43.5	15.2	1.7	22.0	82.4	9.2	8.7	100.3	23.8	11.9	X35.7
8		0.3	43.2	14.4	1.3	22.7	81.6	6.1	16.8	104.5	28.8	12.5	41.3
9	corncob	0	7.8	1.2	0	4.6	13.6	3.1	23.7	40.4	14.7	21.2	35.9
10		0.1	24.1	6.9	1.0	21.4	53.4	7.9	16.1	77.4	20.7	19.5	40.2
11		0.2	33.1	10.5	1.2	23.8	68.6	5.9	12.1	86.6	35.4	16.0	51.4
12		0.3	23.9	8.0	0.8	25.7	58.4	8.1	15.2	81.7	33.1	19.9	53.0
13	wheat straw	0	7.9	2.1	0	1.3	11.3	3.7	14.2	29.2	14.8	9.1	23.9
14		0.1	12.7	3.4	0.6	1.8	18.5	3.8	11.3	33.6	24.0	14.4	38.4
15		0.2	19.9	7.8	1.2	9.9	38.8	8.7	7.2	54.7	21.4	17.6	39.0
16		0.3	16.8	5.3	0.8	11.3	34.2	11.2	7.7	53.1	24.6	14.6	39.2
17	rice straw	0	6.9	1.8	0	4.6	13.3	1.4	22.1	36.8	12.6	8.0	20.6
18		0.1	15.9	4.4	0.8	16.5	37.6	7.8	7.9	53.3	11.7	18.5	30.2
19		0.2	21.2	6.8	1.5	11.6	41.1	9.8	12.7	63.6	18.3	13.8	32.1
20		0.3	14.9	4.5	1.6	16.8	37.8	10.2	11.5	59.5	13.9	20.3	34.2

[a] The reaction conditions were feedstock (1 g), $LiTaMoO_6$ (0.2 g), Ru/C (0.2 g), H_3PO_4 solution (40 mL, different concentrations), 6 MPa H_2 (RT), 24 h, 503 K. [b] For the annotations for products yields, see Table 1.

three abundant carbon sources of raw biomass.[37] Despite its rigidity, high value-added products such as fine chemicals and fuels potentially obtained from lignin should not be underestimated. The carbon content in the lignin was about 65 wt % based on the analysis method of the previous study.[62] In this study, a good yield of lignin derived compounds could be achieved. Based on the source of biomass, the yields varied. The yield could up to 51.4% when corncob was employed as the feedstock (Table 1, entry 9). These compounds included monophenols, hydrocarbons, alcohols, acids and esters (see the Supporting Information). The differences of products might be caused by the different parts of the same plant was used. GC−MS analysis suggested the main monophenols were guaiacols and phenols, specifically 4-alkyl-2-methoxyphenol and *p*-alkylphenol (alkyl:methyl, ethyl and propyl). It suggested that the *β*-O-4 and 4-O-5 bonds with low activity energy were easily broken. Because the hydrogenation reactions were carried out in the catalytic system, it was inevitable that hydrocracking of some monophenols could be performed (Scheme 1, path C). For instance, we found benzene and cyclohexane (cyclohexane was incorporated into other C6A) formed in the gas phase. Also, alcohols such as 2-cyclohexylethanol, 3-cyclohexylpropanol, 3-phenylpropan-1-ol and cyclohexanol were detected, which might be yielded from partial hydrogenation of the monophenols. In addition, these alcohols could be deoxygenated to produce alkylcyclohexanes.[63] For example, through dehydration, allylcyclohexane could be formed from the precursor 3-cyclohexylpropanol; through hydrodeoxygenation, other alkylcyclohexanes such as butylcyclohexane, isopropylcyclohexane, propylbenzene, hexylcyclohexane were also formed. Furthermore, high-energy-density hydrocarbons with increased carbon number (a range of C14−C18:1,2-dicyclohexylethane, 1,3-dicyclohexylpropane, 1,6-dicyclohexylhexane, etc.) were identified by GC−MS analysis. Table 2 shows an example of lignin-derived products from corn stalk. In this case, 23.84% of phenolic monomers, 10.1% of hydrocarbons and 1.8% of other derivatives were achieved after reaction. These results indicated high quality fuels could be potentially obtained from lignin over suitable catalytic system. Compared to the raw biomass, alkali lignin degradation showed a decreased yield of products. This might be caused by the increased solubility of lignin in the intermediates of gasoline fuels from carbohydrate fraction of raw biomass because many reports suggested the importance of organic solvent for lignin degradation.[37] As for the phenolic dimer or oligomer, which might be a significant component of the products,[42] in this paper, GC−MS analysis did not identify these compounds in the ethyl ether phase.

Overall, this catalytic system was not only highly selective to yield gasoline fuels from the conversion of cellulose and hemicellulose but also favored the degradation of lignin to produce value-added chemicals. Intriguingly, with respect to the distribution of lignin derived products, hydrocarbons with a range of C6−C19 products were detected in the liquid phase, which implied the catalytic system could be used for the hydrodeoxygenation of the monophenols. Especially, with the detection of bicyclohexylalkanes, this conversion also showed the potential application of producing jet fuels from lignin through the degradation of raw biomass.

Effect of the Concentration of H_3PO_4 Solution. Proton acid plays an important role in degradation of raw biomass. The hydrolysis of cellulose, hemicellulose and lignin could be efficiently catalyzed using proton acid.[64,65] In addition, the removal of oxygen to yield hydrocarbons could be achieved with the aid of proton acid. As mentioned above, Sels and co-workers used tungstosilicic acid to facilitate the cellulose conversion to gasoline fuels, specifically accelerated the ring-opening of tetrahydrofuran ring.[11] Kou and co-workers demonstrated Ru/C, Pt/C and Rh/C could be used for the degradation of white birch wood lignin with 4.6 wt % yield of monomers and 9.7 wt % yield of dimers in water. With the

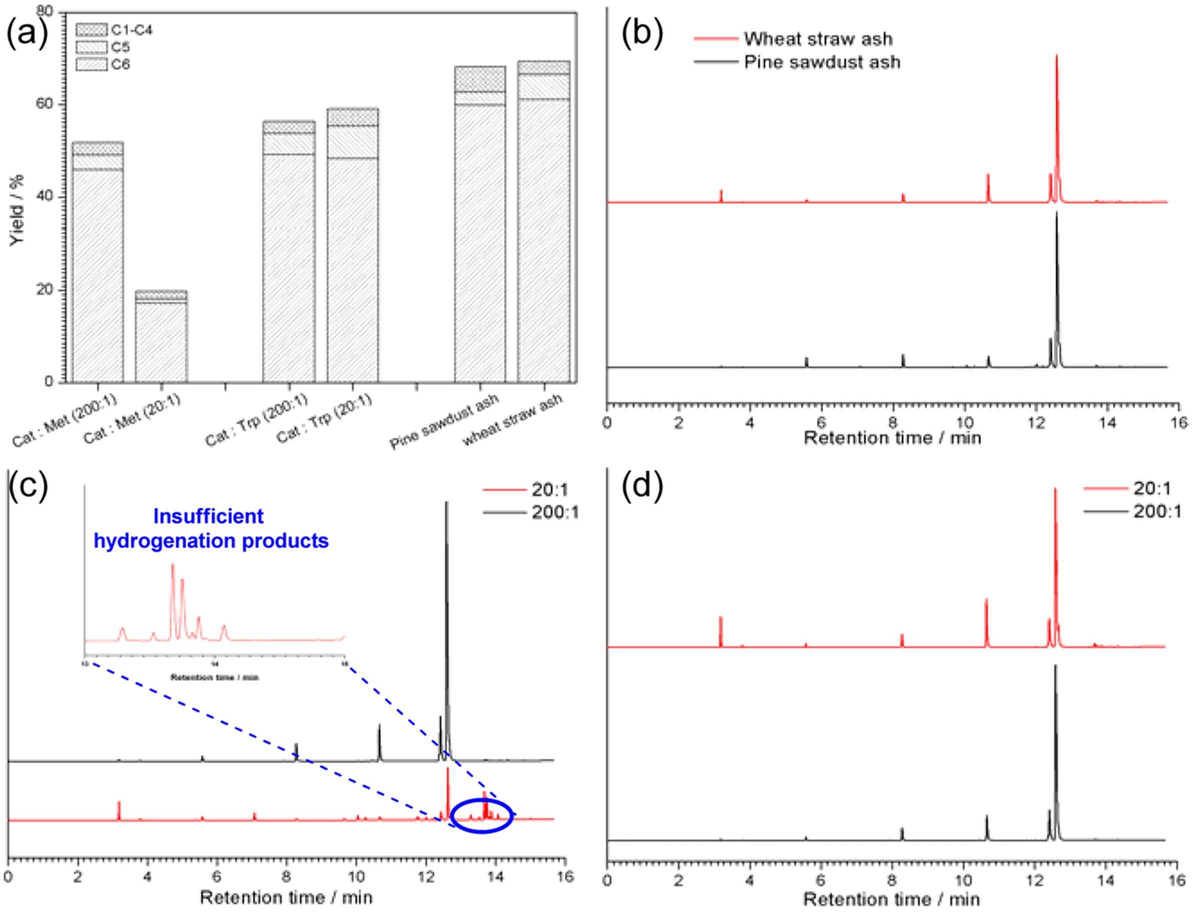


Figure 1. Effect of the addition of different composition from the raw biomass on cellulose conversion. (a) Gas products of cellulose conversion for the addition of different impurities. For Cat (catalyst): Met = 20:1, the yields of insufficient products were included as a fraction of the total hexanes yield. (b) Ratio of catalyst to ash was 10:1 (w/w). (c) Ratios of catalyst to Met were 200:1 and 20:1 (w/w). (d) Ratios of catalyst ($LiTaMoO_6$ and Ru/C) to Trp were 200:1 and 20:1 (w/w). Reaction conditions as in Table 1, entry 2.

addition of H_3PO_4, the yields were improved.[66] This clearly indicated the essential function of proton acid in the conversion of raw biomass.

The effect of H_3PO_4 solution concentration was shown in Table 3. One could find that phosphoric acid was indispensible for the cellulose and hemicellulose conversion for the five kinds of tested raw biomass. Without the addition of phosphoric acid, the yields of hexanes and pentanes were dramatically low, which only gave less than 27% of liquid alkanes (hexanes and pentanes) (Table 3, entries 1, 5, 9, 13 and 17). When H_3PO_4 concentration increased from 0 to 0.2 M, the total yields of liquid alkanes significantly went up. This might be resulted from the enhanced proton acid could facilitate the ring-opening of lactone compounds.[61] However, further increasing of the concentration did not give higher yields. In contrast, the yields were slightly decreased. It might be caused by that the formation of the robust isosorbide is sensitive to high acid concentration, which means high acid concentration would result into the rise of isosorbide yield.[67] For the lignin fraction, the results suggested the depolymerization of lignin was acid concentration dependent. With the rise of H_3PO_4 concentration, all of these tested substrates showed increased yields of phenols and other related products. For corncob, the yield of the lignin degradation products amounted to 53%, which indicated the lesser amount of lignin was easier to be degraded (see Table S2 of the Supporting Information). Note that the deficiency of the mass balance was resulted from some unknown products in the residue that were hard to separate from the residue mixture.

Effect of Biogenic Impurities. On the basis of the above tests of different raw biomass conversion, it was found that the wheat straw and rice straw showed significantly lower yields of liquid alkanes with only about 40% yield of liquid alkanes, though the contents of cellulose and hemicellulose were comparable to those of other three substrates (Table S2 of the Supporting Information). This was probably caused by catalyst deactivation. With respect to catalyst deactivation, one may concern the coke formation on the surface the catalyst and poisoning by biogenic impurities. According to the SEM analysis, no noticeable coke was observed on the surface of catalysts after wheat straw and rice straw conversion (Figure S6 of the Supporting Information). Hence, it was of importance to investigate the compositions of raw biomass, especially the biogenic impurities.

The difference of lignin contents to affect the performance of carbohydrate conversion should be ruled out because the primary lignin units of wheat straw, rice straw, corn stalk and corncob are grass based lignin, though woody lignin (pine sawdust) and grass lignin had different primary units.[68] The reason that catalyst deactivation caused by minerals poison should be excluded. That was because of all these tested

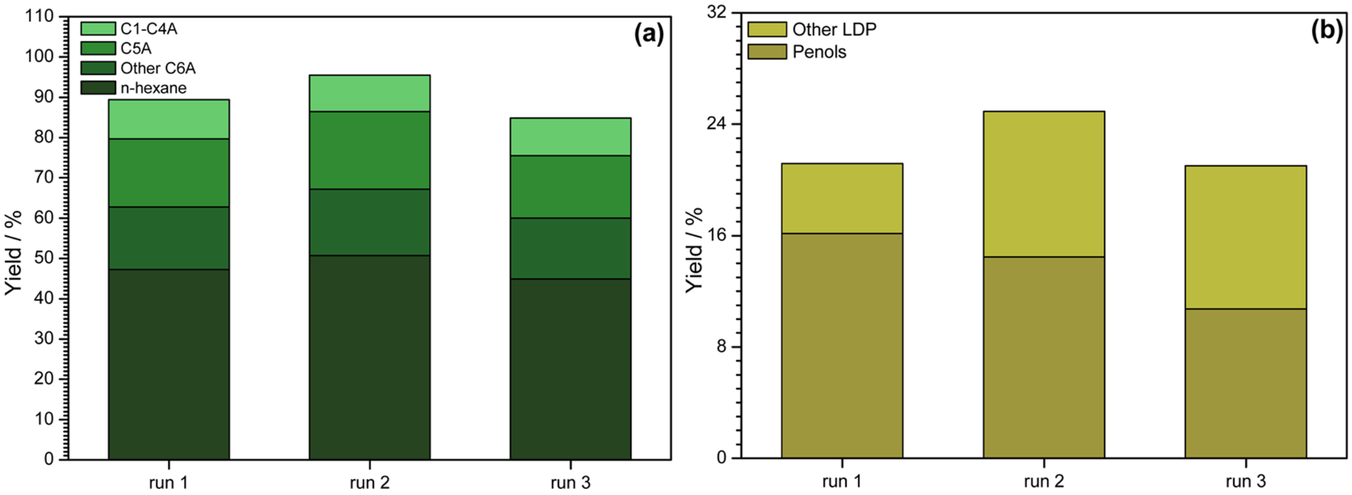


Figure 2. Results of reuse potential test of the catalyst for pine sawdust conversion. Reaction conditions as in Table 1, entry 5.

biomass contained minerals, while only rice straw and wheat straw gave lower yields of gasoline alkanes.

Elemental analysis indicated the significantly different contents of the sulfur (Table S1 of the Supporting Information). In both rice straw and wheat straw, sulfur contents were almost 10 times higher than other three different substrates. Hence, we assumed that sulfur might be the main reason for the poorer performances of rice straw and wheat straw because sulfur was recognized as the poison for metal catalysts.[69,70] Because most of the detected sulfur was from the organic compositions of raw biomass, we deliberately employed methionine (Met, $C_5H_{11}NO_2S$) and tryptophan (Trp, $C_{11}H_{12}N_2O_2$, control group) as the biogenic impurities to investigate the performance of cellulose conversion. It was found that when the ratio of the catalyst ($LiTaMoO_6$ and Ru/C) to amino acid was 200:1, the yields of hexanes only showed a slight decline (Figure 1a). However, with the increased ratio (20:1), different amino acids showed clearly different performances that the hexanes yield sharply declined over the reaction system with Met (from 45.9% to 17.2%, Figure 1a,c), whereas only little difference was detected over that with Trp (from 49.2% to 48.4%, Figure 1a,d). GC and GC−MS analysis showed that a proportion of insufficient hydrogenation products were yielded (Figure 1c, and Figure S9 of the Supporting Information). SEM-EDS analysis also suggested detectable amount of sulfur was deposited on the surface of the catalyst when wheat straw and rice straw was used as the substrate, whereas the data of other feedstocks suggested otherwise (Figure S5F,G,H,I of the Supporting Information). It clearly indicated the sulfur from biogenic impurities had a significantly adverse influence on the catalyst activity. These results agreed with that of Dumesic and co-workers' recent study, which also revealed the side effect of the amino acids with sulfur.[71]

On the other hand, ash might possess inorganic sulfur, which also might pose a negative effect on the activity of catalyst. SEM-EDS confirmed that a small amount of sulfur was remained in wheat straw ash (WSA) and rice straw ash, though no noticeable sulfur was detected on the surface of pine sawdust ash (PSA) (Figure S5L,M,N of the Supporting Information). However, the tests of cellulose conversion suggested the addition of different ashes improved the yields of total liquid alkanes (from 57.7% to 62.8% for WSA, 66.6% for PSA), specifically hexanes (from 53.6% to 60% for WSA, 61.2% for PSA). These results indicated the biomass ash had inherent catalytic activity, which was also confirmed by previous reports.[34,72] Besides that, it also verified that minerals poison was not the reason for low catalytic activity for wheat straw and rice straw conversion because these ashes contained many minerals from biomass.

Hence, we could conclude that no matter what the sources of raw biomass from this study were employed, lignin content and biomass ash did not show noticeable negative effect on the biomass conversion, specifically cellulose conversion. In contrast, the sulfur from amino acid gave apparent side effect on the catalytic activity.

It should be noted that the lignin degradation was less affected by the sulfur content from the biomass, which might be resulted from that the ether bond is easier to break in the hydrothermal condition or acidic medium.[73] Although the production of hexanes from carbohydrates required a deep hydrodeoxygenation process, the activity of solid hybrid catalyst showed its indispensability.

Reuse Potential of the Catalyst. For its potential industry application, vital importance of reuse ability of catalyst should be addressed. Therefore, we employed pine sawdust as the substrate to analyze the recycling potential of the hybrid catalyst. The results were summarized in Figure 2. For the carbohydrate fraction, the catalytic system showed a good reusability that only slight decrease was observed during the third run (from 79.7% to 75.4%). The increased yield of total liquid alkanes (86.4%) in the second run might be ascribed to the remained feedstock from the first test. On the other side, the total yield of lignin degradation products was slightly increased to 24.9% in the second run, and then dropped to 21% for the third run. Collectively, the catalytic system (without H_3PO_4 solution) could be reused for three times (at least) for both carbohydrate and lignin degradation. Notwithstanding the acceptable reusability, the changes of the catalysts should be examined for the potentially commercial application. ICP analysis suggested the total Ru leaching reached 5% after the third run, while no detectable result was found for Ta and Mo leaching and Ru leaching was not detected after the first run. However, FT-IR tests (Figure S3 of the Supporting Information) found that aromatic compounds were deposited on the surface of the catalysts, confirmed with a characteristic wavenumbers of benzene ring (1511, 1460, 728, 714 cm^{-1}).[74] SEM images of the fresh and the recovered catalysts of the third run (Figure S4 of the Supporting Information) demonstrated the tar formation. It should be noted that the tar formation increased with the increasing run numbers which would potentially inhibit the activity of the catalysts. Hence, further attention should be paid to the hydrothermal stability of the catalysts. Nevertheless, the catalytic system already showed the reusability potential for at least three runs without significant loss of activity.

CONCLUSIONS

The feasibility of a one-pot conversion of untreated biomass to gasoline alkanes and value-added chemicals was disclosed by this work in single aqueous phase. For the cellulose and hemicellulose fractions, the main products were hexanes and pentanes. Besides the suggested HMF-to-alkane route and sorbitol route, a lactone route was proved to be an alternative way to produce hexanes. The GCL, MPA and HA conversions suggested they, as the C6 intermediates, could be selectively transformed into hexanes. Lactone compounds such as GCL were selectively converted to hexanes via consecutive ring-opening and hydrodeoxygenation reactions. Hemicellulose had been found that it could be appreciably transformed into pentanes through this versatile catalytic system. In addition, this catalytic system exhibited competitive activity for degradation of lignin fraction of untreated biomass to phenols and C6−C19 hydrocarbons. Furthermore, the catalytic system displayed an acceptable reusability on pine sawdust and the potentially commercial application for hydrocarbon fuels from untreated biomass. The influence of biogenic impurities on catalysts was studied in this study. Ash contains minerals and inorganic sulfur displayed little effect on our catalytic system. In contrast, amino acid with sulfur showed negative effect on catalysts activity, which resulted in dramatic decrease of the yield of hexanes from cellulose conversion.

One may concern down-processing separation of the products. There are many solutions for fractionation of lignocellulose components.[42,75−77] Recently, a lignin-first biorefinery process was developed by the group of Sels. In our case, the gas phase products could be easily separated from the mixture. As for the liquid products, they could be further reduced to biofuel or separated by a distillation process.

For its potential utilization, further improvements are needed to focus on how to inhibit the side effect of the biogenic impurities, optimize the stability of the catalytic system, improve the total yield of gasoline fuels and convert phenols to high-energy-density hydrocarbons.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Characterization of catalysts and biomass, elemental and composition analysis of raw biomass, SEM-EDS analysis, HPLC analysis of aqueous phase products and GC−MS analysis. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.5b00256.

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Notes

The authors declare no competing financial interest.

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